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(54) Deposit easy removable coating fixed to material surface.

(57) A deposit easy removable coating fixed to a material surface, said coating comprising a hydrophilic resin which is swelled with water but is not washed away with water to disappear, and is solid in an air at an ambient temperature, from which any deposit such as a toner ink can be removed with water.

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BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a deposit easy removable coating which is fixed to a surface of material from which the deposit is easily removed with water, whereby the material can be repeatedly cleaned easily.

Description of Related Art

10 Hitherto, it is difficult to remove a water-insoluble deposit from a material surface. For example, a liquid oil should be cleaned by water containing a surfactant with considerable labor, or by an organic solvent which is harmful to human body or environment.

15 Since a waxy or solid deposit is hardly removed using the surfactant, it should be removed by the organic solvent or mechanically scraped off, which requires heavy work. But, such deposit may not be completely removed, or the material to which the deposit is adhered may be damaged. In many cases, the waxy or solid deposit may not be removed.

20 It is possible to remove the deposit by forming a releasable or soluble coating on the material and removing the deposit together with the coating. However, whenever the coating is removed, a fresh coating should be formed, or the removed coating generates an additional waste. Therefore, this technique does not provide an essential solution.

25 As a coating from which the deposit can be repeatedly removed, a coating of polytetrafluoroethylene (hereinafter referred to as "PTFE") (for example, TEFLON™ of DuPont) is known. However, it is not widely used, since it is expensive, a kind of surface on which the PTFE coating can be formed is limited, or it has poor transparency.

30 It is highly desired to develop a coating with which the deposit can be repeatedly removed from the material surface and which solves the above problems.

35 As explained above, to remove the deposit from the material surface, a large amount of work is required, or some methods use the organic solvent which is harmful to the human body and environment. In the case of OHP films or office automation papers such as copying papers, they are used and wasted in a large scale to cause the environmental problem, since an ink cannot be removed from their surfaces. This is because there is no coating from which the deposit such as the ink is repeatedly removed with ease and which is cheap and has good flexibility in use.

35 SUMMARY OF THE INVENTION

An object of the present invention is to provide a coating which is formed on a material surface and from which a deposit can be easily removed using water, whereby the material surface can be easily cleaned.

40 This and other objects are achieved by a deposit easy removable coating fixed to a material surface, said coating comprising a hydrophilic resin which is swelled with water but is not washed away with water to disappear, and is solid in an air at an ambient temperature.

45 When the coating of the present invention is fixed on the material surface, the deposit adhered to the surface can be easily removed from the surface with water.

The coating of the present invention does not prevent adhesion of the deposit, but it allows the adhesion of the deposit. The coating of the present invention is characterized in that the adhered deposit can be removed from the coating only with water.

50 From the coating of the present invention, most of water - insoluble or hardly soluble deposits such as an oily material can be removed. Therefore, the present invention is particularly effective with these deposits.

DETAILED DESCRIPTION OF THE INVENTION

55 The deposit easy removable coating of the present invention should be swelled with water. To effectively remove the deposit, a volume swell is preferably at least 1.5 times. The volume swell herein used is obtained by dipping a sample having a length of about 1 cm, a width of about 1 cm and a thickness of about several ten μm in water for 5 minutes, calculating a ratio of the size (length or width) after dipping to that before dipping, and cubing the calculated ratio.

To repeatedly use the coating, it should not be washed away to disappear. To form such coating, preferably, the resin has a gel content, corresponding to a ratio, of the resin portion which is not dissolved in water and washed away is at least 50 %, more preferably at least 70 %. The resin having such gel content can provide scratch resistance, water resistance and the like to the coating.

5 To this end, it is effective to crosslink the resin. Examples of crosslinkable functional group are an epoxy group, an isocyanate group, a double bond, and the like. The functional group can be present in a crosslinking agent and/or in the resin molecule. As a crosslinking source, a chemical crosslinking agent, such as an epoxy crosslinking agent, an isocyanate crosslinking agent, etc., or irradiation can be used.

10 To suppress the washing away or peeling off of the coating, the coating should have adhesion or release resistance to prevent the removal of coating from the material surface. To this end, it is advantageous to treat the material surface or form a layer of a material which is different from the material to be coated.

15 For example, to improve the adhesion, treatment with or a surface layer of parachlorophenol, trifluoroacetic acid, a silane coupling agent, a titanium coupling agent, an azide compound or a polymer can be employed. When the degrees of swelling of the coating and the material to be coated are different, a surface layer having an intermediate degree of swelling between them can be formed to absorb strain generated therebetween.

20 The coating of the present invention which is fixed to the material surface should contain the resin swellable with water. Such resin has, for example, a polar functional group or a hydrophilic chain. Specific examples of the polar functional group or the hydrophilic chain are a carboxylic acid group, a hydroxyl group, a sulfonic acid group, an amide group, an amino group, a phosphoric acid group or their salts, and a polyethylene glycol chain.

25 Examples of the resin having the above functional group or the hydrophilic chain are homo- or copolymer of acrylic acid, methacrylic acid, vinyl alcohol, hydroxyethyl methacrylate, dihydroxypropyl methacrylate, acrylamido-2-methylpropanesulfonic acid, acrylamide, methacrylamide, N,N-dimethylacrylamide, N-acrylglycinamide, N-isopropylacrylamide, N,N-dimethylaminopropylacrylamide, vinylpyrrolidone, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, allylamine or their salts, quaternary amino compounds, polyethylene glycol, or copolymers of one or more of these monomers with other monomer.

30 The hydrophilicity of the resin can be evaluated by a receding water contact angle. In the present invention, the resin having the receding water contact angle of 40 degrees or less, preferably 20 degrees or less, more preferable 10 degrees or less, in particular, about 0 degree is used advantageously used.

35 The receding water contact angle is measured by forming a water drop on the resin film, sucking water with a syringe, and measuring an angle between the water drop and the resin surface with, for example, a protractor, when the edge of water drop starts to move inwardly.

When the coating is treated with the specific aqueous solution and the hydrophilicity is changed by such treatment, the water contact angle should be measured after the resin is dipped in the aqueous solution and dried.

40 To improve various properties of the coating, it is possible to use components in combination with the hydrophilic resin. For example, the coating composition may optionally contain inorganic powder, a plasticizer, an antistatic agent, a lubricant, a dye or pigment, a dispersant, a hydrophobic resin and the like.

The present invention makes it possible to remove the deposit with water from the material surface. Therefore, when the deposit is removed by cleaning with water, the present invention is effectively practiced. When the resin is not sufficiently swelled only with water so that the removal of deposit is difficult, or the removing efficiency of deposit is improved by increasing the swelling rate of the resin, the use of water containing an electrolyte, an alcohol or the like is effective in most cases.

45 As the electrolyte, a salt, a base or an acid is suitably used depending of the kind of resin. Examples of the electrolyte are sodium bicarbonate, sodium chloride, acetic acid, potassium hydroxide, sodium hydroxide, hydrochloric acid, sulfuric acid, nitric acid, and the like. Examples of alcohol are methanol, ethanol, isopropanol, and the like.

50 By the use of a water-soluble resin, it is possible to supply a component or components which is or are contained in the resin and eluted by water, whereby the properties of coating can be maintained. To increase a removing efficiency of deposit, a surfactant and the like can be added to water for cleaning.

55 When water which is used in the removing step is discarded as such or may contact directly to the human body, a component which is contained in water or eluted from the coating is preferably one having less adverse influence on the human body and environment, more preferably a biodegradable component.

The deposit easy removable coating of the present invention should be in the solid state in an air at an ambient temperature to maintain its shape. In view of practical use, the coating in a dry state has a scratch

strength is preferably 6B or harder, more preferably 2B or harder in a pencil scratching test under a load of 100 g. Practically, it is preferable that the coatings do not stick or adhere each other when they are contacted.

5 In some applications, the coating of the present invention is transparent preferably. In such case, the coating preferably has a transmission of at least 80 % with the entire light or a light having a wavelength of 550 nm.

When a substrate to be coated is in the sheet form, the coating of the present invention finds wide variety of application. For example, the coating is used for receiving an ink as the deposit. This is one of the typical examples in which the present invention has good effects. In particular, when the ink is adhered to 10 the substrate, for example a sheet of paper, by copying, typewriting or printing, the present invention is very much effective to decrease an amount of waste paper.

15 These days, the amount of waste paper generated by printing with printing machines, typewriting with a printer or a typewriter, or printing is considerably increasing. According to the present invention, the coating has compatibility with the ink used in the above application fields, so that ink images can be formed on the coating. Therefore, the use of coating of the present invention for removal of the ink is very advantageous.

It is advantageous that the coating of the present invention can cope with the toner used in an 20 electrophotographic type copier or a laser beam type printer among the above application fields in view of the amount of paper sheets used in the offices these days.

Of course, it is also advantageous that the coating of the present invention is cope with the ink used in 25 other type of typewriting or printing. Examples of the ink are ink-jet printing ink, thermal printing ribbon ink, impact printing ink, typewriter ribbon ink and the like.

In these cases, the coating on the substrate material preferably has heat resistance and mechanical strength so that it is not deteriorated before and after the provision of the ink by copying, typewriting or printing.

25 As a sheet form substrate, a resin film, a paper sheet, a metal foil or their composite or laminate is suitably used. The sheet form substrate has flexibility and a thickness sufficient for copying, typewriting or printing, and maintains flatness before and after the deposition and removal of the ink. That is, the substrate material preferably has heat resistance, water resistance, mechanical properties or shape memory which makes is possible to maintain the flatness.

30 Preferably, the coating has a shrinkage factor or an expansion factor which makes it possible to maintain the flatness before and after the deposition of the ink by copying, typewriting or printing and removal of the ink. When the coatings are formed on both surfaces of the sheet form substrate, it is possible to use the coatings having a wide range of the shrinkage factor or expansion factor. Preferably, the flatness to be maintained is such that, when the sheet is placed on a flat surface, a height of the most risen 35 part of the sheet is not larger than 10 mm.

A thickness of the coating of the present invention is preferably from 0.05 μm to 5 μm , more preferably from 0.1 μm to 3 μm . When the thickness is too small, the number of repeated use is decreased. When it is too large, the coating tends to be damaged when the deposit is removed.

35 The coating of the present invention can be formed on the substrate material by a conventional method for forming a resin coating on the material. For example, a solution or suspension of the resin is applied on the material surface and dried.

The deposit easy removal coating of the present invention which is fixed to the material surface should be swelled with water. In a specific application, for example, the deposition of the above described ink, it is practically preferred that the coating is swelled to a necessary extent in a specific temperature range. That 45 is, at room temperature, the deposit is adhered to the coating but hardly removed, while the deposit is easily removed in the removing step at a temperature different from the room temperature. The removal temperature of higher than 20 $^{\circ}\text{C}$ is suitable for the use of coating and also for designing the removing step. A temperature of 28 $^{\circ}\text{C}$ or higher is more preferred.

40 Examples of the resin which achieves the above effect, resins having a nitrogen-containing group and/or an organic acid group, or mixtures thereof. Examples of the nitrogen-containing group and organic acid group are an amide group, an amino group, a carboxylic acid group, and the like. Examples of the resins having such functional group and the mixture thereof are homo- or copolymers of acrylamide, methacrylamide, N,N-dimethylacrylamide, N-acrylglycinamide, N-isopropylacrylamide, N,N-dimethylaminopropylacrylamide, vinylpyrrolidone, acrylic acid, methacrylic acid, etc., copolymer of one or 55 more of the above monomers with other monomers, and mixtures thereof.

Typical examples are polyacrylic acid, polyacrylamide, a mixture of polyacrylic acid and polyacrylglycinamide, and a mixture of polyacrylic acid and polydimethylacrylamide. In the case of polyacrylamide, the swelling in the molecule level in the presence of water at a temperature higher than 29 $^{\circ}\text{C}$ was proved

(see Hiroki Katono et.al, "HYOMEN" (Surface), 30 (1992) 30).

It is preferred that the ink is deposited on the coating with a specific writing means including copying, typewriting and printing and removed from the coating.

The deposit easy removal coating of the present invention fixed to the material surface and comprising the hydrophilic resin which is swelled with water but not washed away by water and does not disappear, and is solid in the air at room temperature can be widely used for the purpose of removal of deposit. For example, the coating of the present invention can be used in the following applications.

To remove the ink, the coating is formed on the OHP sheet, a sheet of paper or paper-like material, a celluloid picture sheet, and the like.

To remove stains such as oil, the coating can be formed on building materials, furniture, ventilation equipments, kerosene heaters, electric appliances, gas equipments, tools, tablewares or other daily necessities. In particular, the coating is effectively used in places which are stained by oils, paints, and the like, for example, a kitchen, a workshop where a machine is used or a paint is applied.

For masking purpose, the coating of the present invention can be used in a painting step or preparation of graphics. In view of good hydrophilicity of the resin which is swelled with water, the coating can be used as an anti-fogging film.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be explained further in detail by the following examples.

In Examples, as deposits, there were used a machine oil which is relatively easily removed and a toner ink which is baked in the copying process by an electrophotographic type copier and most firmly adhered to the substrate material among the deposits.

25 Example 1

A composition of the following components was charged in a flask equipped with a condenser and reacted at 80 °C while stirring till increase of viscosity was observed:

| 30 | Component | Parts by weight |
|----|---|-----------------|
| | Polyethylene glycol (MW = 1000) | 10 |
| | Crosslinking agent (adduct of trimethylolpropane with 3 moles of tolylene diisocyanate) | 9.7 |
| 35 | Cyclohexanone | 23 |
| | Toluene | 23 |

The resulting resin solution was coated in a wet thickness of 60 µm on a polyethylene terephthalate film having a thickness of 100 µm and dried, followed by treatment at 70 °C for 3 days to obtain a deposit easy removable film which consisted of the crosslinked hydrophilic resin and was fixed to the substrate material.

40 Separately, the resulting resin solution was coated on a releasing paper in a wet thickness of about 200 µm and dried, followed by treatment at 70 °C for 3 days to prepare a sample for measuring a volume swell and a gel content. Water was used as a treating liquid in the removal step of toner ink and the measurements of volume swell and gel content.

45 Example 2

A composition of the following components was mixed at room temperature to obtain a resin solution:

| 50 | Component | Parts by weight |
|----|---|-----------------|
| | Commercially sold hydrophilic resin (A copolymer of acrylic acid salt (?) and vinyl alcohol in a weight ratio of 4:6) | 10 |
| | Crosslinking agent (tetrafunctional epoxy compound with a tertiary amine group in a molecule) | 0.025 |
| 55 | Isopropanol | 7.6 |

The resulting resin solution was coated in a wet thickness of 300 μm on a polyethylene terephthalate film having a thickness of 100 μm and dried, followed by treatment at 110 $^{\circ}\text{C}$ for 5 hours to obtain a deposit easy removable film which consisted of the crosslinked hydrophilic resin and was fixed to the substrate material.

5 Separately, the resulting resin solution was coated on a TEFLONTM sheet adhered on a glass plate in an amount of 25 g per 100 cm^2 and dried, followed by treatment at 110 $^{\circ}\text{C}$ for 5 days to prepare a sample for measuring a volume swell and a gel content. Water was used as a treating liquid in the removal step of toner ink and the measurements of volume swell and gel content.

10 Example 3

A composition of the following components is charged in a flask equipped with a condenser and reacted under nitrogen stream at 70-80 $^{\circ}\text{C}$ for 10 hours while stirring to obtain a 15 wt. % solution of a hydrophilic resin A in isopropanol.

| | Component | Parts by weight |
|----|-------------------------------------|-----------------|
| | Methacrylic acid | 9 |
| | Acrylic acid | 1 |
| 20 | 2-Hydroxyethyl methacrylate | 13 |
| | Acrylamide | 1 |
| | N,N-Dimethylaminoethyl methacrylate | 1 |
| | Azobisisobutyronitrile | 0.38 |
| 25 | Isopropanol | 142 |

Then, the following mixture was mixed at room temperature to obtain a resin solution:

| | Component | Parts by weight |
|----|---|-----------------|
| 30 | Solution of Resin A in isopropanol | 10 |
| | Crosslinking agent [a mixture of glycidylether of glycerin, glycidylether of polyethylene glycol (ethylene glycol = ca. 4 moles) and polyethylene glycol-glycidyl ether of sorbitol in a weight ratio of 8:1:1] | 0.075 |

35 The resulting resin solution was coated in a wet thickness of 60 μm on a polyethylene terephthalate film having a thickness of 100 μm , a surface of which was treated to with polyurethane (easy adhesion treatment) and dried, followed by treatment at 110 $^{\circ}\text{C}$ for 5 hours to obtain a deposit easy removable film which consisted of the crosslinked hydrophilic resin and was fixed to the substrate material.

40 Separately, the resulting resin solution was coated on a releasing paper in a wet thickness of about 350 μm and dried, followed by treatment at 110 $^{\circ}\text{C}$ for 5 hours to prepare a sample for measuring a volume swell and a gel content. A 1 wt. % aqueous solution of sodium bicarbonate was used as a treating liquid in the removal step of toner ink and the measurements of volume swell and gel content.

45 Example 4

In the same manner as in Example 3 except that an aqueous solution containing 1 % by weight of the resin A and 1 % by weight of sodium bicarbonate was used as a treating liquid in the removal step of toner ink and the measurements of volume swell and gel content, the experiments were carried out.

50 Comparative Example 1

In the same manner as in Example 1 except that no deposit easy removal film was formed on the polyethylene terephthalate film, the experiments were carried out.

Comparative Example 2

5 A 5 wt. % aqueous solution of a commercially sold resin (a copolymer of an acrylic acid salt and vinyl alcohol in a weight ratio of 4:6) was coated in a wet thickness of 120 μm on a polyethylene terephthalate film having a thickness of 100 μm and dried, followed by treatment at 110°C for 5 hours to form a coating of the resin which was not crosslinked substantially.

10 Separately, the resulting resin solution was coated on a TEFLON™ sheet adhered on a glass plate in an amount of 14 g per 100 cm^2 and dried, followed by treatment at 110°C for 5 days to prepare a sample for measuring a swell and a gel content. Water was used as a treating liquid in the removal step of toner ink and the measurements of volume swell and gel content.

Comparative Example 3

15 In the same manner as in Example 3 except that, as a substrate film on which the deposit easy removal film was formed, a polyethylene terephthalate film which had not been surface treated was used, the deposit easy removal film was formed. The same treating liquid as used in Example 3 was used in the removal step of toner ink and the measurements of volume swell and gel content.

20 On the deposit easy removal film obtained in each of Examples 1-4 and Comparative Examples 2 and 3 or the film of Comparative Example 1, the machine oil was applied with a brush in an area of about 1 cm x 2 cm, or characters of the toner ink were copied by the electrophotographic type copier. As the characters, 25 12 points Gothic alphabet characters were printed. When the resin A was used, the substrate film carrying the deposit easy removal film was dipped in the treating liquid for 20 minutes and dried before the application of machine oil or copying of the characters, since the hydrophilicity of the coated film was improved by the treating liquid. Then, the removability of machine oil or copied characters and other properties were evaluated as follows:

Volume Swell

30 The sample for measuring the volume swell is cut to a size of about 1 cm x 1 cm and dipped in the treating liquid for 5 minutes. From the measured sizes before and after dipping, a ratio of the side length is calculated and cubed to obtain a volume swell.

Gel Content

35 About 0.1 g of the sample is weighed, dipped in 50 ml of the treating liquid and subjected to the ultrasonic wave (frequency: ____ Hz) for 30 minutes. Then, the treating liquid is changed and the same procedure is repeated. The undissolved portion of the sample was dried at 80°C till no weight change is observed (about one week). From the weight difference before and after the above treatment, a weight percentage of the undissolved portion is calculated as a gel content.

Receding Water Contact Angle

40 A water drop is formed on the film surface, water is sucked with a syringe, and an angle between the water drop and the film surface with is measured with a protractor, when the edge of water drop starts to move inwardly.

Pencil Scratching Test

45 The pencil scratching test is carried out according to JIS K 5400 except that a load is changed to 100 g.

Sticking-Adhesion Test

50 The coated surfaces of a pair of substrate films are laminated and kept standing for one day with placing a weight of 1 kg at the center of the films to evaluated the sticking and adhesion properties. The sticking and adhesion are ranked as "O" (neither sticking nor adhesion is observed), "Δ" (sticking is observed) or "X" (adhesion is observed).

Light Transmission

Using a UV-visible light spectrophotometer (200-20 Type Double Beam Spectrophotometer manufactured by Hitachi), a light transmission at a wavelength of 550 nm is measured.

5

Maintenance of Flatness

After copying the characters using a electrophotographic type copier (NP 5060 manufactured by Canon), the film is placed on a flat surface and the height of most risen part of the film is measured.

10

Deterioration of Coating

After five times removal of the deposit, a condition of coating is observed with naked eyes or an optical microscope.

15

Removability of Machine Oil

The surface of each film is wiped with a sponge for photography in running water to check the removability of machine oil and ranked as "OO" (removed with running water only), "O" (completely removed with gentle wiping) or "X" (with strong wiping, the machine oil is not removed but is spread).

Removability of Toner Ink

After each film is dipped in the treating liquid for 20 minutes, a surface of the film is wiped with a sponge for photography in running water to check the removability of toner ink and ranked as "OO" (removed with running water only), "O" (completely removed with gentle wiping) or "X" (not removed with strong wiping).

Repeated Removability of Toner Ink

30 After carrying out the procedure in the above test of removability of toner ink, water is thoroughly removed with a hair dryer, and copying of the characters with toner ink and their removal are repeated, and the number of copies while the toner ink is completely removed is counted.

The results are shown in Tables 1 and 2.

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50

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Table 1

| Property | Example 1 | Example 2 | Example 3 | Example 4 |
|---|------------------|------------------|-----------------|------------------|
| Volume swell (times) | 2 | 50 | 11 | --- |
| Gel content (%) | 95 | 60 | 90 | --- |
| Receding water contact angle (°) | 15 | <5 | <5 | --- |
| Pencil scratch test | B | 2H | 4H | --- |
| Sticking-adhesion test | Δ | ○ | ○ | --- |
| Light transmission (%) | 77 | 86 | 86 | --- |
| Maintenance of flatness (mm) | 0 - 4 | 0 - 7 | 0 - 4 | --- |
| Deterioration of coating after 5 removals | Substantially no | Substantially no | Minute cracking | Substantially no |
| Removability of machine oil | ○ | ○○ | ○○ | ○○ |
| Removability of toner ink | ○ | ○ | ○○ | ○○ |
| Repeated removability of toner ink | 5 - 15 | 10 - 20 | 10 - 20 | >20 |

Table 2

| Property | Co. Ex. 1 | Co. Ex. 2 | Co. Ex. 3 |
|---|-----------|---|-----------|
| Volume swell (times) | 1 | Not measurable | --- |
| Gel content (%) | 100 | 0 | --- |
| Receding water contact angle (°) | 60 | --- | --- |
| Pencil scratch test | >4H | --- | --- |
| Sticking-adhesion test | ○ | --- | --- |
| Light transmission (%) | 88 | --- | --- |
| Maintenance of flatness (mm) | 0 - 3 | --- | --- |
| Deterioration of coating after 5 removals | --- | Whole coating was dissolved after one removal | |
| Removability of machine oil | X | ○○ | ○○ |
| Removability of toner ink | X | ○○ | ○○ |
| Repeated removability of toner ink | 0 | 1 | 1 |

As seen from the results in Tables 1 and 2, the deposit easy removal coatings which were formed on the substrate material according to the present invention (Examples 1-4) had better removability of toner ink or better repeated removability of toner ink than the films of Comparative Examples 1-3 having no deposit easy removable coating of the present invention.

Since the deposit easy removable coating of the present invention is effective for removing and repeatedly removing the toner ink, it is of course effective for other deposits.

Claims

1. A deposit easy removable coating fixed to a material surface, said coating comprising a hydrophilic resin which is swelled with water but is not washed away with water to disappear, and is solid in an air at an ambient temperature.
5
2. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said resin has a volume swell of at least 1.5 times.
10
3. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said resin has a gel content of at least 50 %.
15
4. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said resin is crosslinked.
15
5. The deposit easy removable coating fixed to a material surface according to claim 4, wherein said resin is crosslinked through a functional group selected from the group consisting of an epoxy group, an isocyanate group and a double bond.
20
6. The deposit easy removable coating fixed to a material surface according to claim 5, wherein said resin is crosslinked with a crosslinking source selected from the group consisting of an epoxy crosslinking agent, an isocyanate crosslinking agent and irradiation.
25
7. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said resin has a polar functional group or a hydrophilic chain.
30
8. The deposit easy removable coating fixed to a material surface according to claim 7, wherein said polar functional group or hydrophilic chain is selected from the group consisting of a carboxylic acid group, a hydroxyl group, a sulfonic acid group, an amide group, an amino group, a phosphoric acid group or their salts, and a polyethylene glycol chain.
35
9. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said resin has a receding water contact angle of not larger than 40 degrees.
40
10. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said material is a material a surface of which is treated to improve adhesiveness or release resistance, or a material having a surface layer with adhesiveness or release resistance.
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11. The deposit easy removable coating fixed to a material surface according to claim 10, wherein said surface treating is carried out with or said surface layer is made of an acid, a coupling agent or a polymer.
50
12. The deposit easy removable coating fixed to a material surface according to claim 1 to 11, which is swellable with water containing an electrolyte.
55
13. The deposit easy removable coating fixed to a material surface according to claim 12, wherein said electrolyte is selected from the group consisting of a salt, a base and an acid.
14. The deposit easy removable coating fixed to a material surface according to claim 1, which is swellable with water containing an alcohol.
15. The deposit easy removable coating fixed to a material surface according to claim 1, which is maintained by water containing a water-soluble resin.
16. The deposit easy removable coating fixed to a material surface according to claim 1, which further comprises at least one additive selected from the group consisting of inorganic powder, a plasticizer, an antistatic agent, a lubricant, a dye, a pigment, a dispersant and a hydrophobic resin.
55

17. The deposit easy removable coating fixed to a material surface according to claim 1, which has a hardness of at least 6B measured by a pencil scratch test under a load of 100 g in a dry state.
18. The deposit easy removable coating fixed to a material surface according to claim 1, which does not stick or adhere to each other.
19. The deposit easy removable coating fixed to a material surface according to claim 1, which is transparent.
20. The deposit easy removable coating fixed to a material surface according to claim 19, which has a light transmission of at least 80 % with the entire light or a light having a wavelength of 550 nm.
21. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said material is in the sheet form.
22. The deposit easy removable coating fixed to a material surface according to claim 21, wherein said sheet form material is a material selected from the group consisting of a resin film, a paper sheet, a metal foil, and their composite and laminate.
23. The deposit easy removable coating fixed to a material surface according to claim 21, which is compatible with an ink used in copying, typewriting or printing.
24. The deposit easy removable coating fixed to a material surface according to claim 23, wherein said ink is a toner ink.
25. The deposit easy removable coating fixed to a material surface according to claim 23, wherein said ink is an ink selected from the group consisting of an ink-jet printing ink, a thermal printing ribbon ink, an impact printing ink and a typewriter ribbon ink.
26. The deposit easy removable coating fixed to a material surface according to claim 21, wherein said coating has heat resistance and mechanical properties sufficient for preventing deterioration of said coating before and after deposition of said ink.
27. The deposit easy removable coating fixed to a material surface according to claim 21, wherein said material has flexibility and a thickness sufficient for copying, typewriting or printing.
28. The deposit easy removable coating fixed to a material surface according to claim 21, wherein said material has heat resistance, water resistance, mechanical properties or shape memory which makes it possible to maintain flatness before and after deposition of said ink.
29. The deposit easy removable coating fixed to a material surface according to claim 21, wherein said coating has a shrinkage factor or expansion factor which makes it possible to maintain flatness before and after deposition of said ink and removal of said ink.
30. The deposit easy removable coating fixed to a material surface according to claim 28 or 19, wherein said flatness is 10 mm or less in terms of a height of most risen part of said material when said material is placed on a flat place.
31. The deposit easy removable coating fixed to a material surface according to claim 1, which has a thickness of 0.05 to 5 μm .
32. The deposit easy removable coating fixed to a material surface according to claim 1, wherein said resin has sufficient swellability in a specific temperature range.
33. The deposit easy removable coating fixed to a material surface according to claim 32, wherein said specific temperature range is at least 20 $^{\circ}\text{C}$.

34. The deposit easy removable coating fixed to a material surface according to claim 32, wherein said resin is at least one resin having at least one group selected from the group consisting of a nitrogen-containing group and an organic acid group.
- 5 35. The deposit easy removable coating fixed to a material surface according to claim 34, wherein said nitrogen - containing group and said organic acid group are an amide group, an amino group and a carboxylic acid group.

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㉓ Deposit easy removable coating fixed to material surface.

㉔ A deposit easy removable coating fixed to a material surface, said coating comprising a hydrophilic resin which is swelled with water but is not washed away with water to disappear, and is solid in an air at an ambient temperature, from which any deposit such as a toner ink can be removed with water.

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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int.Cl.) | | | | | | |
|---|--|--|---|-----------------|-----------------------------------|----------|-----------|---------------|--------------|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | | | | | | | |
| X | FR-A-2 391 784 (UNILEASE) * page 1, line 35 - page 6, line 39; claims * | 1-8 | C09D5/00 | | | | | | |
| X | US-A-5 093 396 (CALHOUN ET AL) * column 2, line 37 - column 6, line 25; claims * | 1 | | | | | | | |
| P, X | WO-A-93 01243 (ALLIED-SIGNAL) * page 4, line 6 - page 9, line 26; claims 1-7 * | 1 | | | | | | | |
| A | EP-A-0 162 611 (ICI) * page 2, line 28 - page 8, line 10; claim 1 * | 1 | | | | | | | |
| A | US-A-4 200 671 (KRAJEWSKI ET AL) ----- | | | | | | | | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.) | | | | | | |
| | | | C09D | | | | | | |
| <p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of compilation of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>12 April 1995</td> <td>Bourgonje, A</td> </tr> </table> | | | | Place of search | Date of compilation of the search | Examiner | THE HAGUE | 12 April 1995 | Bourgonje, A |
| Place of search | Date of compilation of the search | Examiner | | | | | | | |
| THE HAGUE | 12 April 1995 | Bourgonje, A | | | | | | | |
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